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(21) International Application Number: PCT/US00/07865 (22) International Filing Date: 24 March 2000 (24.03.00) (30) Priority Data: 60/129,736 16 April 1999 (16.04.99) US (71) Applicant (for all designated States except US): THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Mid- land, MI 48674 (US). (72) Inventors; and (73) Inventors/Applicants (for US only): SHICK, Reed, A. [US/US]; 2470 E. Newcastle Lane, Midland, MI 48640 (US). TUCKER, Christopher, J. [US/US]; 6232 Fairway Pines Court 2, Bay City, MI 48706 (US). CONRAD, Daniel, C. [US/US]; 5767 Echo Ridge, Stevensville, MI 49085 (US). KOVICH, Mark, B. [US/US]; 491 Ansley, St. Joseph, MI 49127 (US). WRIGHT, Tremitchell [US/US]; 51832 Hedge Lane, Granger, IN 46530 (US). (74) Agent: HILL, Stanley, K.; Intellectual Property, P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW. ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: METHOD AND COMPOSITION FOR REDUCED WATER DAMAGE LAUNDRY CARE (57) Abstract A method and composition for laundering a cloth article having reduced water damage in which a solvent having competing adsorption is employed in the method and composition, including a method of determining whether a candidate solvent for use in the method and composition is acceptable.		

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METHOD AND COMPOSITION FOR REDUCED WATER DAMAGE LAUNDRY CARE

This invention relates to the use of certain solvents, particularly organically-based solvents, in a method for laundering clothes or fabrics so that the process provides the feature of reducing the damage done to fibers in the cloth caused by water. Further, a composition is provided to use in the method featured. Finally, there is provided a means for solvent selection according to which a candidate solvent for use in the composition and the laundry method can be selected.

Numerous patents and publications, too many to cite herein, have dealt with the laundry process, but usually from the standpoint of cleaning. The focus of this invention is the reduction of water damage to clothing and fabric which is washed in the normal wash cycle of commercial or home laundry machines. Some fabrics and clothing are shrunk beyond their intended use by water if, inadvertently, they are included in an aqueous laundry process. Such clothing and fabric can only be adequately cleaned by the solvent based dry-cleaning process. However, such a process can be expensive and is not available for home use. It would therefore be quite an advantage to have a home laundry process that could be useful to clean clothing and fabrics subject to water damage, and particularly shrinkage, in a cost-effective, time effective process with reduced water damage. The present invention has the feature that it will reduce water damage, especially shrinkage as well as wrinkling, dye fading, dye transfer, loss of sizing, pilling, felting, fiber weakening and relaxation. While a reduction of any one of these is considered advantageous, reducing the shrinkage and pilling of wool and the shrinkage and spotting on silk and rayon are major advantages.

The features of the invention are provided in a method of laundering a cloth article in an aqueous admixture so that water damage is avoided by contacting the cloth article in the presence of water with a solvent having a competing adsorption with water on the cloth article. Another aspect of this invention provides an aqueous laundry composition for reduced water damage to a laundered cloth article which comprises an adsorbent amount of at least one solvent or blend of solvents which has competing adsorbency with water on the cloth article. In a still further aspect of this invention, there is provided a method of determining suitability of a solvent for use in a reduced water damage laundry composition and method of laundering a cloth article which comprises the steps of

- A) measuring the surface energy of a fiber to be laundered using the Hansen total solubility parameters and finding the radius of interaction of said fiber;
- 5 B) determining the Hansen total solubility parameters and radius of interaction of a candidate solvent;
- C) determining the Hansen total solubility parameters and radius of interaction of water;
- D) comparing the Hansen total solubility parameters and radius of interaction of said solvent with that of said fiber so that a sphere generated by the radius of interaction of the solvent intersects the sphere generated by the radius of interaction of the fiber
- 10 to obtain a combined fiber/solvent relative difference in the two radii;
- E) comparing the Hansen total solubility parameters and radius of interaction of said water with that of said fiber so that a sphere generated by the radius of interaction of water intersects the sphere generated by the radius of interaction of the fiber to obtain a combined fiber/water relative difference in the two radii; and
- 15 F) comparing the result of said step D with the result of said step E, such that an acceptable solvent for said reduced water damage laundry composition has a combined fiber/solvent relative difference 1.5 times or less than the combined fiber/water relative difference.

20 The method for laundering clothing or fabrics according to the present invention protects the fibers in the cloth by preferentially wetting the cloth fibers. However, the wetting takes place on the fiber surface and, thus, prevents the water from contacting and absorbing into the fiber causing water damage. As used in this invention the term water damage refers to shrinkage, wrinkling, dye fading, dye transfer, loss of sizing, pilling, felting,

25 fiber weakening and fiber relaxation. However, many of these types of damage require repeated washing to manifest the damage. In contrast, shrinkage can be seen in only one wash cycle and many of the remaining water damage effects will be manifest in the same cloth after several washings. Therefore, shrinkage water damage is the most important and immediate type of damage. It is also easily measured by standard laboratory tests which

30 correlate well to effects in actual usage.

Without intending to limit the invention to any theory of operation or mechanism of action, it is believed that by preferentially adsorbing on the surface of the cloth fiber a solvent selected for such characteristics, the absorbency of water into the fiber is hindered and, thus, damage caused by water is decreased. This feature is obtained by the method

35 of laundering a cloth article in an aqueous admixture whereby water damage to the cloth

article is decreased compared to that caused by laundering in water alone, the method comprising contacting the cloth article with a solvent having a competing adsorption on the cloth article and in the presence of water. Adsorption means contact and adhesion of a thin layer of molecules to the surface of a solid body or liquid. Absorption, in contrast, connotes the liquid taking into the bulk of the cloth fiber.

The solvent used in this invention can be selected from the group consisting of aliphatic alcohol, alkylene glycol, alkylene glycol ether, a weak acid or the ester or anhydride of a weak acid, alkylene amine, alkanolamine and aromatic alcohol. Typical of aliphatic alcohols are lower alkyl alcohols such as methanol, ethanol, propanol; unsaturated alcohols, such as, allyl alcohol; cyclic aliphatic alcohols, such as, furfuryl alcohol; and aralkyl alcohols, such as benzyl alcohol. Typical of alkylene glycols are the group consisting of ethylene glycol, propylene glycol, diethylene glycol and triethylene glycol. Non-limiting examples of alkylene glycol ethers are selected from the group consisting of ethylene glycol methyl ether, ethylene glycol ethyl ether, butylene glycol methyl ether, diethylene glycol ethyl ether, diethylene glycol methyl ether, propylene glycol phenyl ether and propylene glycol methyl ether. Typical of the weak acids, esters or anhydrides are those selected from the group consisting of formic acid, acetic acid, lactic acid, acetic anhydride, methyl lactate, ethyl lactate, propyl lactate, butyl lactate and glycol ether acetate. The typical examples of alkylene amines useful in this invention are selected from the group consisting of ethylenediamine and diethylenetriamine. A preferred alkanolamine is monoethanolamine. Typical of useful aromatic alcohols are those selected from the group consisting of phenol, cresol and resorcinol.

The solvent is contacted with the cloth article in an amount sufficient to reduce or decrease water damage. Because of the different solubility parameters of various fabrics and fibers and the different solvents involved the amount of solvent can be greatly varied. In addition, the temperature of laundering, the amount of agitation and the overall amount of water employed can influence the amount of solvent necessary to reduce or decrease water damage in the method of this invention. In general, it has been found that from about 0.1 to about 15 percent by weight of solvent based on the total weight of the aqueous wash solution or liquid can be used. Preferably, from 1 to about 10 percent by weight of solvent is used, with from about 3 to about 5 percent by weight being most preferred amounts of solvent useful in this invention.

The method of laundering contemplated by the present invention does not rely on any particular type of laundry apparatus and any typical commercial or household washing machine can be usefully employed. Of course, cleaning, while important, is not the

emphasis of the present invention. Other laundry additives can be employed as are typically useful in laundry operations for cleaning. As is common in such wash applications, the water and solvent are usually combined prior to addition of cloth. Alternatively, the wash liquor, including the solvent can be applied to the cloth in the form of a spray, foam, mist, vapor, immersion, absorbent transfer or by other means. Once applied, mechanical action is used to wash the cloth, fabric, fiber or clothing. After thorough agitation the bulk of the liquid and soil are extracted from the cloth. An additional bulk wash step with the aqueous wash liquor can be carried out and then one or more rinse steps can be employed. The cloth is then dried according to conventional practice, such as by tumble, microwave, convection, reduced pressure, air hang, absorbent or other means of drying.

In a still further aspect of this invention, there is provided an aqueous laundry composition which provides reduced water damage to a laundered cloth article and which comprises an adsorbent amount of at least one solvent or blend of solvents which has competing absorbency with water on the cloth article, clothing, fabric or fiber to be laundered. More particularly, the composition of this invention is described in which the solvent has competing adsorption on the article in relation to water and is non-absorbent on the cloth, clothing, fabric or fiber to be laundered. One of the methods which is useful to determine whether a solvent can be employed in the method and composition of this invention takes advantage of the Hansen total solubility parameters, the radius of interaction and the relative distance of a sphere generated by the radius of interaction calculated in accord with certain equations derived by Hansen. These parameters are used to determine whether a solvent will compete with water to adsorb on the fiber surface, preventing contact with water and, therefore, reducing water damage to the fiber, fabric or cloth. The Hansen solubility parameters are discussed in Chapter 4 of Industrial Solvents Handbook (by Wesley Archer, Marcel Dekker, Inc. publisher), (1996), pages 35-56, which are incorporated by reference as if fully set forth, with respect to the solubility of solvents in resins. Dr. Wesley J. Archer applied the Hansen solubility parameter theory in reformulating solvent-based coatings in an article in American Paint & Coatings Journal, March 2, 1992, pages 38-45, which is incorporated herein by reference as if fully set forth. These articles form the basis for a further aspect of the invention which is a method of determining a suitable solvent for use in a reduced water damage laundry composition which comprises the steps of (A) measuring the surface energy of a fiber to be laundered using the Hansen total solubility parameters and finding the radius of interaction of the fiber; (B) determining or obtaining the Hansen total solubility parameters and radius of interaction of a candidate solvent; (C) determining or obtaining the Hansen total solubility parameters and radius of

interaction of water; (D) comparing the Hansen total solubility parameters and radius of interaction of the candidate solvent with that of the fiber so that a sphere generated by the radius of interaction of the fiber intersects with a sphere generated by the radius of interaction of the solvent to obtain a combined fiber solvent relative difference in the two radii of interaction; (E) comparing the Hansen total solubility parameters and radius of interaction of water with those of the fiber so that a sphere generated by the radius of interaction of water intersects the sphere generated by the radius of interaction of the fiber to obtain a combined fiber/water relative difference in the two radii of interaction; and (F) comparing the result of step (D) with the result of step (E) such that an acceptable solvent for the reduced water damage laundry composition of this invention has a combined fiber/solvent relative difference 1.5 times or less than the combined fiber/water relative difference. Also, the candidate solvent should have less absorbency than water so as not to cause fiber damage itself from absorption in the fiber.

Having set forth the general description of the invention, it is now desired to set forth the best mode of carrying out the present invention with respect to the following Examples of the invention in comparison to damage caused by water or by water and a popular standard laundry detergent.

EXAMPLES

Cloth fiber damage can be demonstrated as dimensional stability. Dimensional stability can be reported as the percent shrinkage of a cloth after washing treatment. Square cloth pieces, approximately 30 cm on each side were marked with a square pattern approximately 25 cm each side with a Laundry Sharpie marker. The cloth pieces were then washed in a laboratory scale horizontal axis laundry machine. The machine was charged with two liters of wash liquor, followed by the test cloth. The cloth was washed for three minutes at 200 rpm tumble agitation with tumble direction reversals every 30 seconds. The wash liquor was drained and then extracted from the cloth with an 1800 rpm spin cycle for one minute. Two liters of rinse water was added and the cloth again agitated at 200 rpm for one minute. The rinse water was drained and then extracted from the cloth with an 1800 rpm spin cycle for one minute. Air-dry the test cloth. Measure the test pattern dimensions, then iron the cloth with a dry iron at the recommended temperature setting, and re-measure the test pattern. Shrinkage was reported as average percent difference from the dimensions of the unwashed and washed test cloth. For comparison wash data for a pure solvent dipropylene glycol n-butyl ether without a water rinse was included.

Acetate

Wash Liquor	% Shrinkage
(weight percent)	(average)

5	100%	Water			2.6%
	95.4%	Water	4.4%	Tide	2.5%
	95%	Water	5%	Methanol	1.7%
	95%	Water	5%	diethylene glycol	1.2%
	100%	dipropylene glycol n-butyl ether			0.0%

10

Silk

Wash Liquor	% Shrinkage
(weight percent)	(average)

15	100%	Water			4.0%
	95.4%	Water	4.4%	Tide	4.4%
	95%	Water	5%	n-methyl pyrrolidone	2.1%
	100%	dipropylene glycol n-butyl ether			0.1%

20 Rayon (not ironed)

Wash Liquor	% Shrinkage
(weight percent)	(average)

25	100%	Water			10.0%
	95.4%	Water	4.4%	Tide	9.8%
	95%	Water	5%	diethylenetriamine	4.9%
	100%	dipropylene glycol n-butyl ether			0.2%

Wool

Wash Liquor				% Shrinkage
(weight percent)				(average)
5	100%	Water		5.2%
	95.4%	Water	4.4% Tide	5.2%
	95%	Water	5% diethylenetriamine	3.9%
	100%	dipropylene glycol n-butyl ether		0.1%

- 10 From the above Examples it is clear that shrinkage is reduced when a solvent is used according to the present invention in an aqueous laundry composition. The invention can also be seen to include the method in which the solvent retards the adsorption and absorption of water on the cloth article or fiber by the solvent itself adsorbing on the fiber or cloth article preferentially. A still further aspect of the invention involves the solvent being
- 15 defined as having competing adsorption on the cloth article in relation to water and the solvent being non-absorbent on the fiber or cloth article. More preferably, the solvent is selected from those having a radius of interaction with the fiber or cloth article which is about 1.5 times or less than the radius of interaction of water with the fiber or cloth article, preferably, the radius of interaction is 1.0 times or less than the radius of interaction of water
- 20 with the fiber or cloth article.

CLAIMS:

1. A method of laundering a cloth article in an aqueous admixture whereby water damage to said article is decreased, said method comprising contacting said article in the presence of water with a solvent having a competing adsorption on said article.

2. The method of Claim 1 wherein said solvent retards the adsorption and absorption of water on said article by adsorbing on said article preferentially.

3. The method of Claim 1 wherein said solvent has competing adsorption on said article in relation to water and is non-absorbent on said article.

4. The method of Claim 3 wherein said solvent has a radius of interaction with said article which is about 1.5 times or less than the radius of interaction of water with said article.

5. The method of Claim 4 wherein said solvent is selected from the group consisting of aliphatic alcohol, alkylene glycol, alkylene glycol ether, weak acid or the ester or anhydride of a weak acid, alkylene amine, alkanolamine and aromatic alcohol.

6. The method of Claim 5 wherein said solvent is an aliphatic alcohol which is selected from the group consisting of methanol, ethanol, allyl alcohol, propanol, furfuryl alcohol and benzyl alcohol.

7. The method of Claim 5 wherein said solvent is an alkylene glycol which is selected from the group consisting of ethylene glycol, propylene glycol, diethylene glycol and triethylene glycol.

8. The method of Claim 5 wherein said solvent is an alkylene glycol ether which is selected from the group consisting of ethylene glycol methyl ether, ethylene glycol ethyl ether, butylene glycol methyl ether, diethylene glycol ethyl ether, diethylene glycol methyl ether, propylene glycol phenyl ether and propylene glycol methyl ether.

9. The method of Claim 5 wherein said solvent is a weak acid or ester or anhydride of a weak acid selected from the group consisting of formic acid, acetic acid,

lactic acid, acetic anhydride, methyl lactate, ethyl lactate, propyl lactate, butyl lactate and glycol ether acetate.

10. The method of Claim 5 wherein said solvent is an alkylene amine which is
5 selected from the group consisting of ethylenediamine and diethylenetriamine.

11. The method of Claim 5 wherein said solvent is an alkanolamine which is
monoethanolamine.

10 12. The method of Claim 5 wherein said solvent is an aromatic alcohol which is
selected from the group consisting of phenol, cresol and resorcinol.

13. The method of Claim 3 in which said solvent is present in a water damage
reduction amount in the laundry solution for laundering said article.

15 14. The method of Claim 13 in which said solvent is present at from about 0.1 to
about 15 percent by weight of the total laundry solution.

20 15. The method of Claim 14 in which said solvent is present at from about 1 to
about 10 percent by weight of the total laundry solution.

16. The method of Claim 15 in which said solvent is present at from about 3 to
about 5 percent by weight of the total laundry solution.

25 17. The method of Claim 1 wherein said article is selected from wool, acetate,
silk and rayon.

18. The method of Claim 17 wherein said article is wool and said solvent is
propylene glycol phenyl ether.

30 19. The method of Claim 17 wherein said article is acetate and said solvent is
methanol.

35 20. The method of Claim 17 wherein said article is acetate and said solvent is
diethylene glycol.

21. The method of Claim 17 wherein said article is silk and said solvent is N-methyl pyrrolidone.

5 22. The method of Claim 17 wherein said article is rayon and said solvent is diethylenetriamine.

23. An aqueous laundry composition providing reduced water damage to a laundered cloth article, said composition comprising an adsorbent amount of at least one
10 solvent or blend of solvents which has competing adsorbency with water on said article to be laundered than water.

24. The composition of Claim 23 wherein said solvent has competing adsorption on said article in relation to water and is non-absorbent on said article.

15 25. The composition of Claim 24 wherein said solvent has a radius of interaction with said article which is about 1.5 to 0.5 times or less than the radius of interaction of water with said article.

20 26. The composition of Claim 25 wherein said solvent is selected from the group consisting of aliphatic alcohol, alkylene glycol, alkylene glycol ether, weak acid or the ester or anhydride of a weak acid, alkylene amine, alkanolamines and aromatic alcohol.

25 27. The composition of Claim 26 wherein said solvent is an aliphatic alcohol which is selected from the group consisting of methanol, ethanol, allyl alcohol, propanol, furfuryl alcohol and benzyl alcohol.

28. The composition of Claim 26 wherein said solvent is an alkylene glycol which is selected from the group consisting of ethylene glycol, propylene glycol, diethylene glycol
30 and triethylene glycol.

29. The composition of Claim 26 wherein said solvent is an alkylene glycol ether which is selected from the group consisting of ethylene glycol methyl ether, ethylene glycol ethyl ether, butylene glycol methyl ether, diethylene glycol ethyl ether, diethylene glycol
35 methyl ether, propylene glycol phenyl ether and propylene glycol methyl ether.

30. The composition of Claim 26 wherein said solvent is a weak acid or ester or anhydride of a weak acid selected from the group consisting of formic acid, acetic acid, lactic acid, acetic anhydride, methyl lactate, ethyl lactate, propyl lactate, butyl lactate and glycol ether acetate.

31. The composition of Claim 26 wherein said solvent is an alkylene amine which is selected from the group consisting of ethylenediamine and diethylenetriamine.

32. The composition of Claim 26 wherein said solvent is an alkanolamine which is monoethanolamine.

33. The composition of Claim 26 wherein said solvent is an aromatic alcohol which is selected from the group consisting of phenol, cresol and resorcinol.

34. The composition of Claim 23 in which said solvent is present at from about 0.1 to about 15 percent by weight of the total laundry solution.

35. The composition of Claim 34 in which said solvent is present at from about 1 to about 10 percent by weight of the total laundry solution.

36. The composition of Claim 35 in which said solvent is present at from about 3 to about 5 percent by weight of the total laundry solution.

37. A method of determining a suitable solvent for use in a reduced water damage laundry composition which comprises the steps of

- A) measuring the surface energy of a fiber to be laundered using the Hansen total solubility parameters and finding the radius of interaction of said fiber;
- B) determining the Hansen total solubility parameters and radius of interaction of a candidate solvent;
- C) determining the Hansen total solubility parameters and radius of interaction of water;

- 5 D) comparing the Hansen total solubility parameters and radius of interaction of said solvent with that of said fiber so that a sphere generated by the radius of interaction of the solvent intersects the sphere generated by the radius of interaction of the fiber to obtain a combined fiber/solvent relative difference in the two radii;
- 10 E) comparing the Hansen total solubility parameters and radius of interaction of said water with that of said fiber so that a sphere generated by the radius of interaction of water intersects the sphere generated by the radius of interaction of the fiber to obtain a combined fiber/water relative difference in the two radii; and
- 15 F) comparing the result of said step D with the result of said step E, such that an acceptable solvent for said reduced water damage laundry composition has a combined fiber/solvent relative difference 1.5 times or less than the combined fiber/water relative difference.

38. The method of Claim 37 wherein said candidate solvent further has less absorbency than water.

INTERNATIONAL SEARCH REPORT

Int. J. Application No.

PCT/US 00/07865

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D7/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D 006L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	claims 1, 9-11, 15; example 2	15, 16, 34-36
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A	claims; example 3	13-16, 34-36
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A	page 8, line 24 - line 26; examples 1, 2	13-16, 34-36
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

20 July 2000

Date of mailing of the international search report

31/07/2000

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INTERNATIONAL SEARCH REPORT

Int. l. Application No.

PCT/US 00/07865

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	abstract	13-16, 34-36
X	US 3 701 627 A (GRUNEWALDER WERNER) 31 October 1972 (1972-10-31)	1-6, 8, 17, 19, 23-27, 29
A	column 2, line 39 - line 48; claim 1; example 1	13-16, 34-36
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A	column 8, line 2 - line 9; claim 1; examples A-G	13-16, 37, 38
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Information on patent family members

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